Supporting Information

Internal charge transfer dependent solvent effect in V-shaped azacyanines

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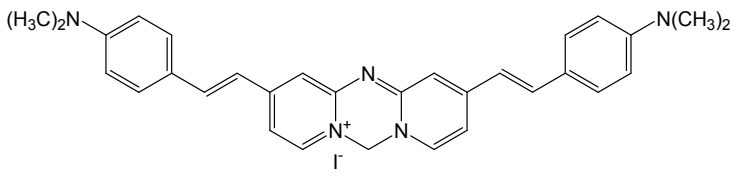
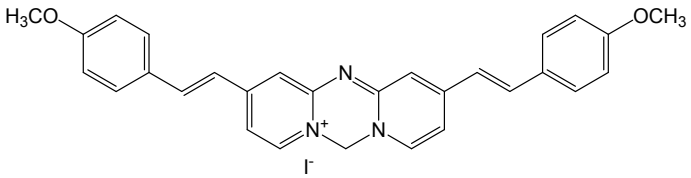
General information

All calculations were done with aid of the Gaussian 09 package.[1] Our intention was to make a direct comparison of calculated/observed properties of compounds **4** and **5** with properties of previously published bis(styryl)azacyanines. ref. 23 main text **Hence, for use of this SI, we decided to give separate numbers to previously described compounds, as it is listed below**:



compound 6



compound 7

Spectroscopic data

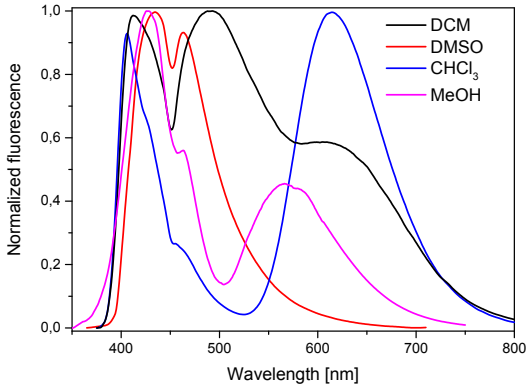


Fig. S1. Normalized fluorescence emission spectra for **4** in all studied solvents (λ_{ex}=350 nm).

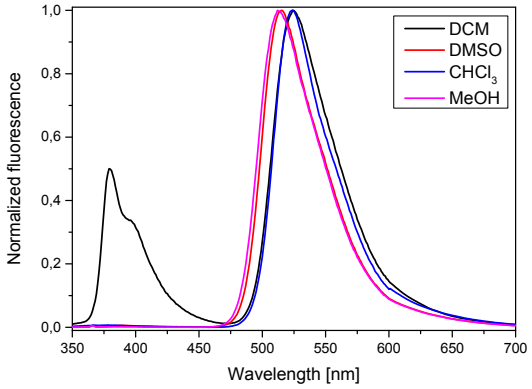


Fig. S2. Normalized fluorescence emission spectra for **5** in all studied solvents (λ_{ex}=330 nm).

Table S1. Optimized ground-state geometry (DFT B3LYP/6-31G(d,p)) of azacyanines **4** and **5** in comparison with previously published bis-styrylazacyanines **6** and **7** (see General information).

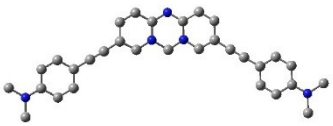
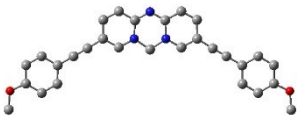
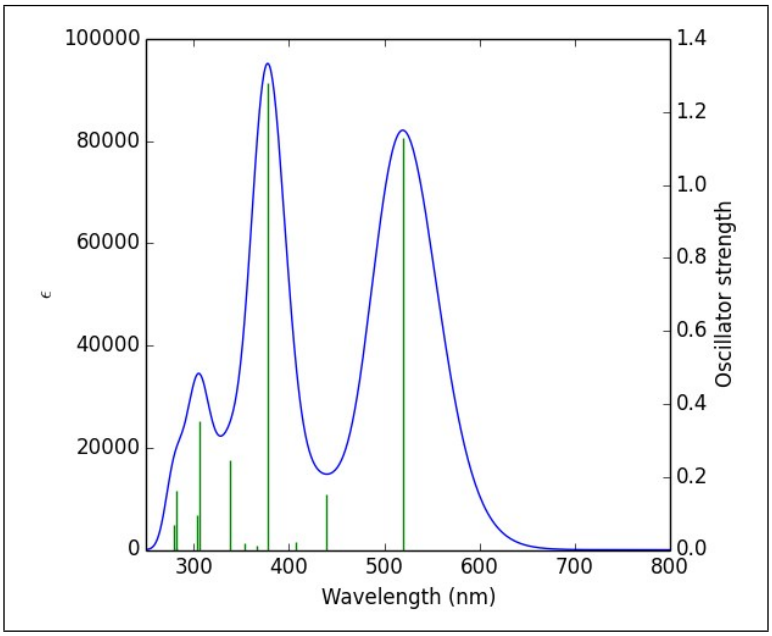
Compd		Compd	
4		**6**	
5		**7**	

Table S2. $S_0 \rightarrow S_1$ transition energies (λ_{abs}) and oscillator strengths (f) calculated for azacyanines **4-7** in different solvents. δq represents charge transferred from D groups to A in $S_0 \rightarrow S_1$ transition (see Table 3, main text of the manuscript). ΔS_1T_n represents the energy gap between the S_1 state and closest lower lying triplet state T_n.

Compd. (solvent)	δq(A)	λ_{abs} (nm)	oscillator strength	ΔS_1T_n (cm^{-1})
4 (isolated)	-0.346	712.2	0.458	
4 (heptane)	-0.410	667.6	0.647	
4 (CH_2Cl_2)	-0.464	610.9	0.955	4 (n=2)
4 (DMSO)	-0.461	598.6	1.036	104 (n=2)
5 (isolated)	-0.329	569.2	0.582	
5 (CH_2Cl_2)	-0.311	519.6	1.130	734 (n=2)
5 (DMSO)	-0.306	514.1	1.206	690 (n=2)
6 (DMSO)	-0.252	593.4	2.567	2566 (n=2)
7 (DMSO)	-0.195	514.5	2.447	549 (n=3)

Table S3. $S_1 \rightarrow S_0$ transition energies (λ_{flu}) and oscillator strengths (f) calculated for compounds **4** and **5** in different solvents. The estimation of Stokes shift is based on the results given in Table 2 and 3. k_r represents estimated rate constant of radiative decay.

Compd. (solvent)	λ_{em} (nm)	oscillator strength	Stokes shift (cm^{-1})	k_r (s^{-1})
4 (Heptane)*	766.1 875.0	0.568 0.001	1925 3549	$6.45 \cdot 10^7$ $8.71 \cdot 10^4$
4 (CH_2Cl_2)	694.2	0.933	1964	$1.28 \cdot 10^8$
4 (DMSO)	681.0	1.034	2021	$1.49 \cdot 10^8$
5 (CH_2Cl_2)	567.0	1.290	1608	$2.67 \cdot 10^8$



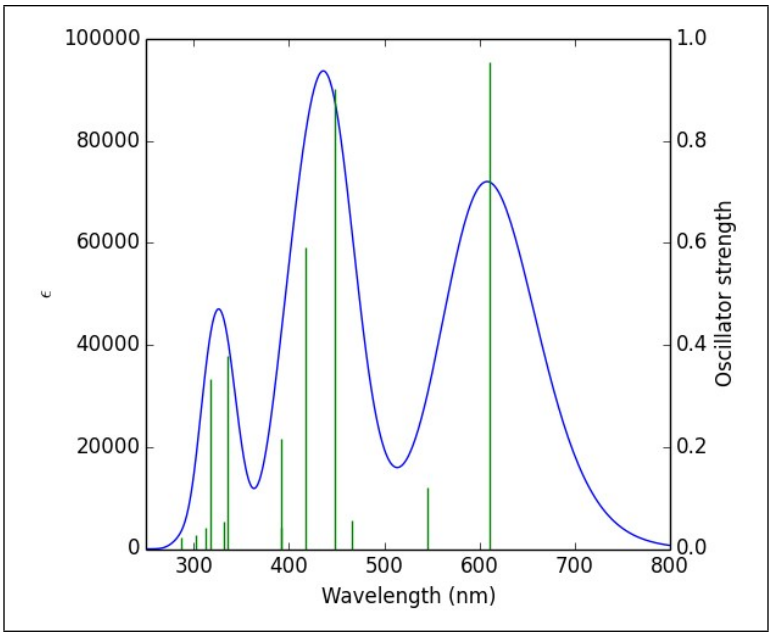
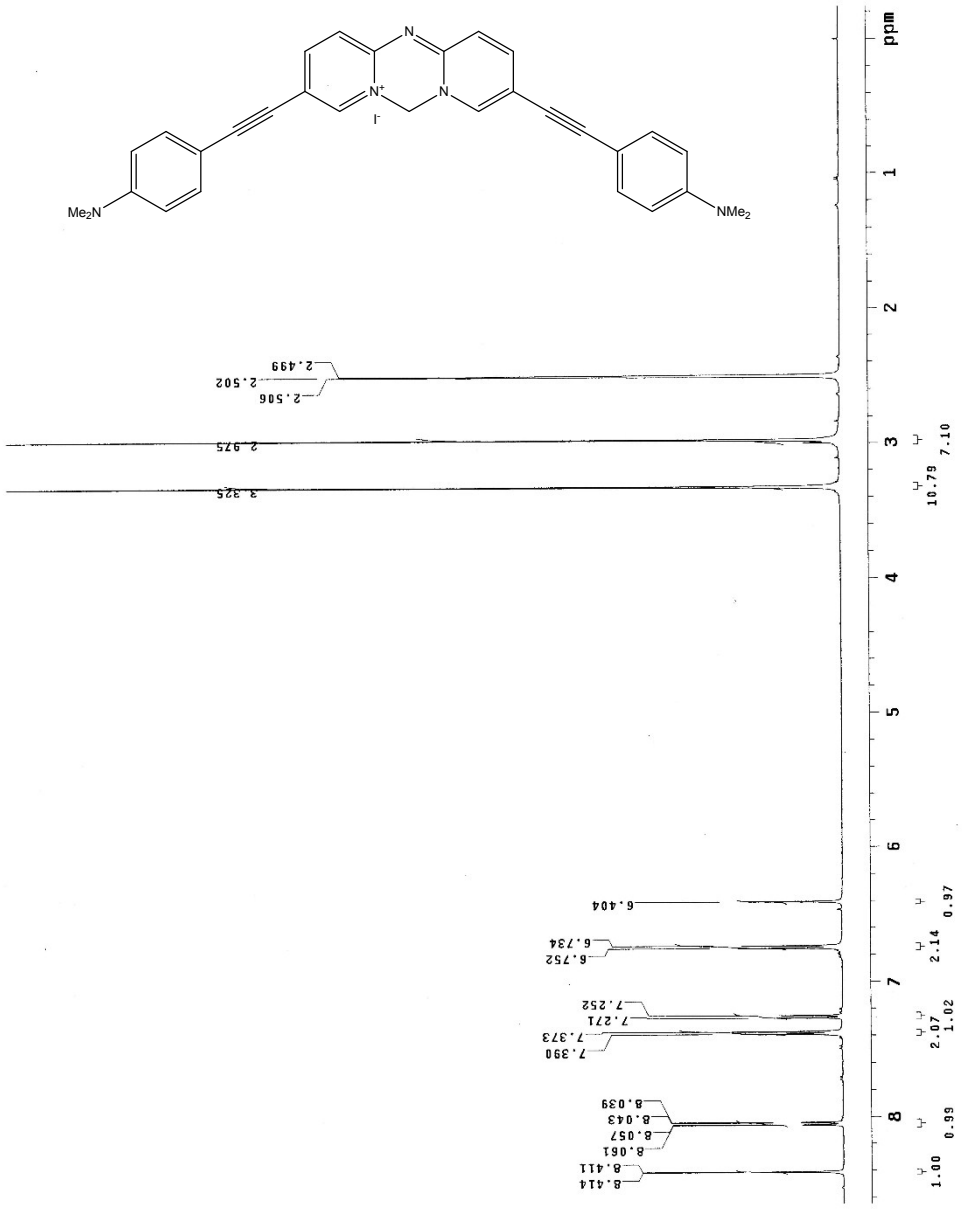


Fig. S3. Simulation (with use of GaussSum 3.0[2]) of the absorption spectra of **5** (top) and **4** (bottom) in CH_2Cl_2.


Me2N
NMe2
N
N+
N
I-
ppm
1
2
3
4
5
6
7
8
2.499
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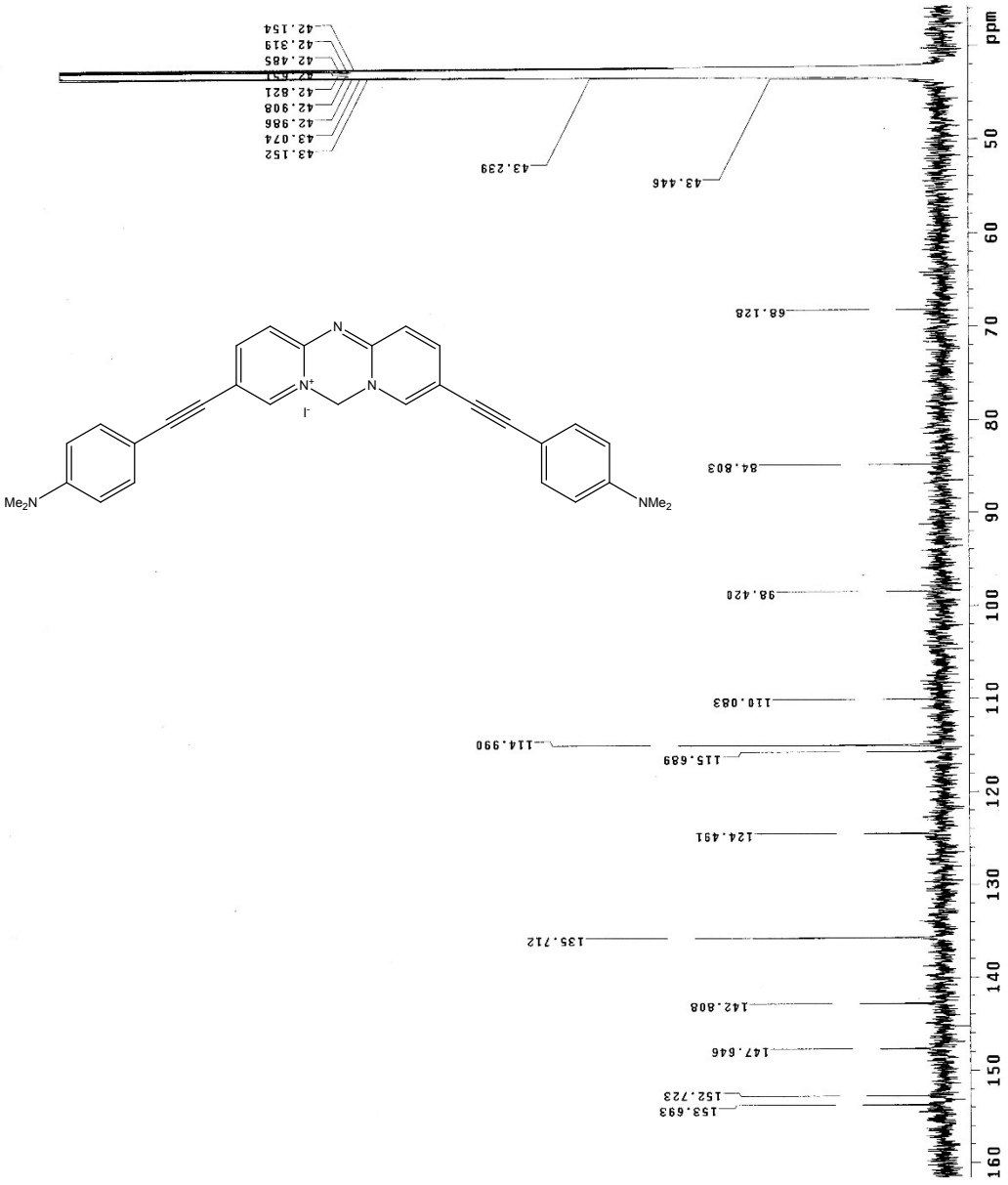
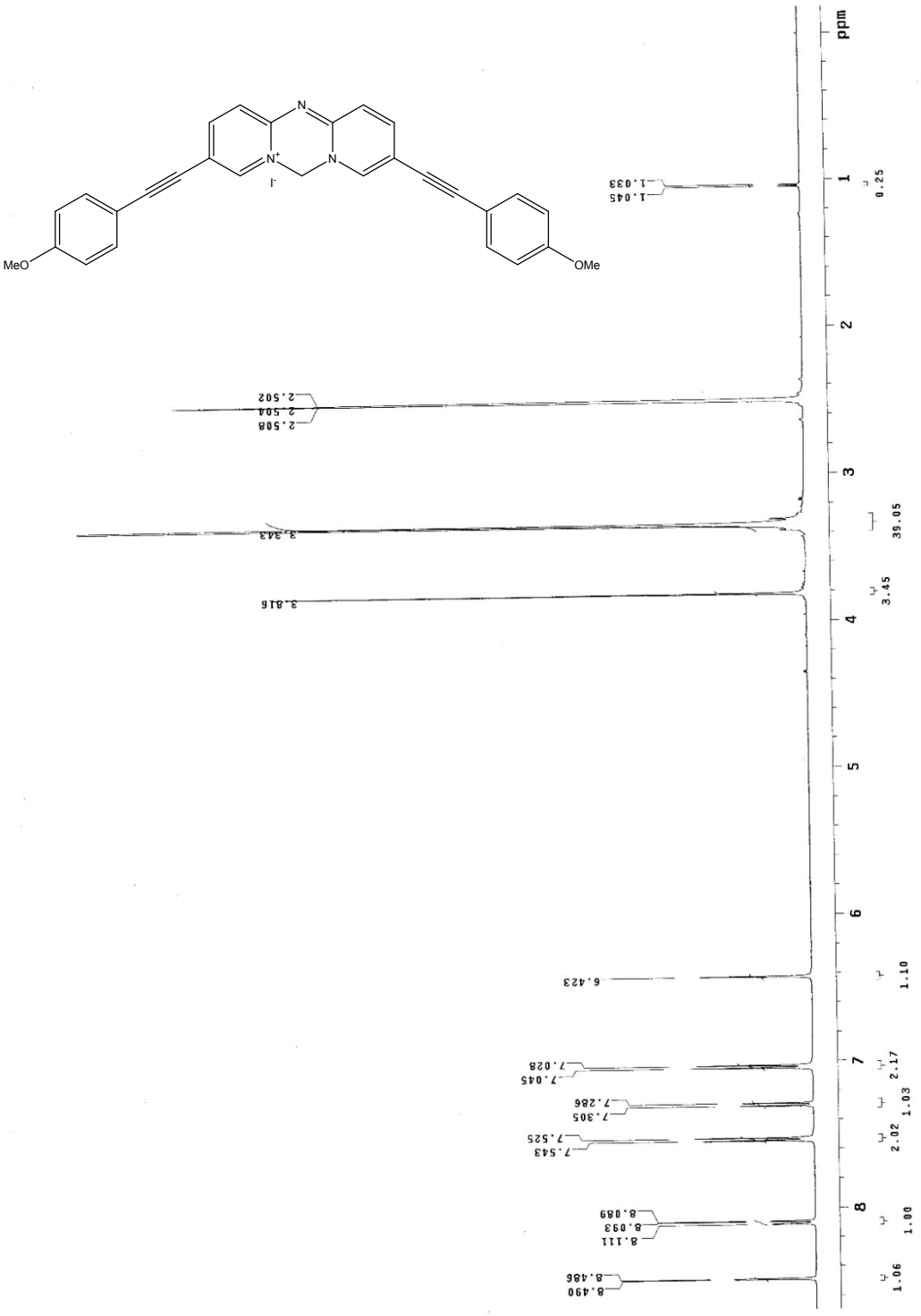
2.506
2.975
3.325
6.404
6.734
6.752
7.252
7.271
7.373
7.390
8.039
8.043
8.057
8.061
8.411
8.414
10.79
7.10
1.00
0.99
2.07
1.02
2.14
0.97


42.154
42.319
42.485
42.821
42.908
42.986
43.074
43.152
43.239
43.446
68.128
84.803
98.420
110.083
114.990
115.689
124.491
135.712
142.808
147.646
152.723
153.693
ppm
50
60
70
80
90
100
110
120
130
140
150
160
N
N+
N
I-
Me2N
NMe2


MeO
OMe
N
N
N+
I-
ppm
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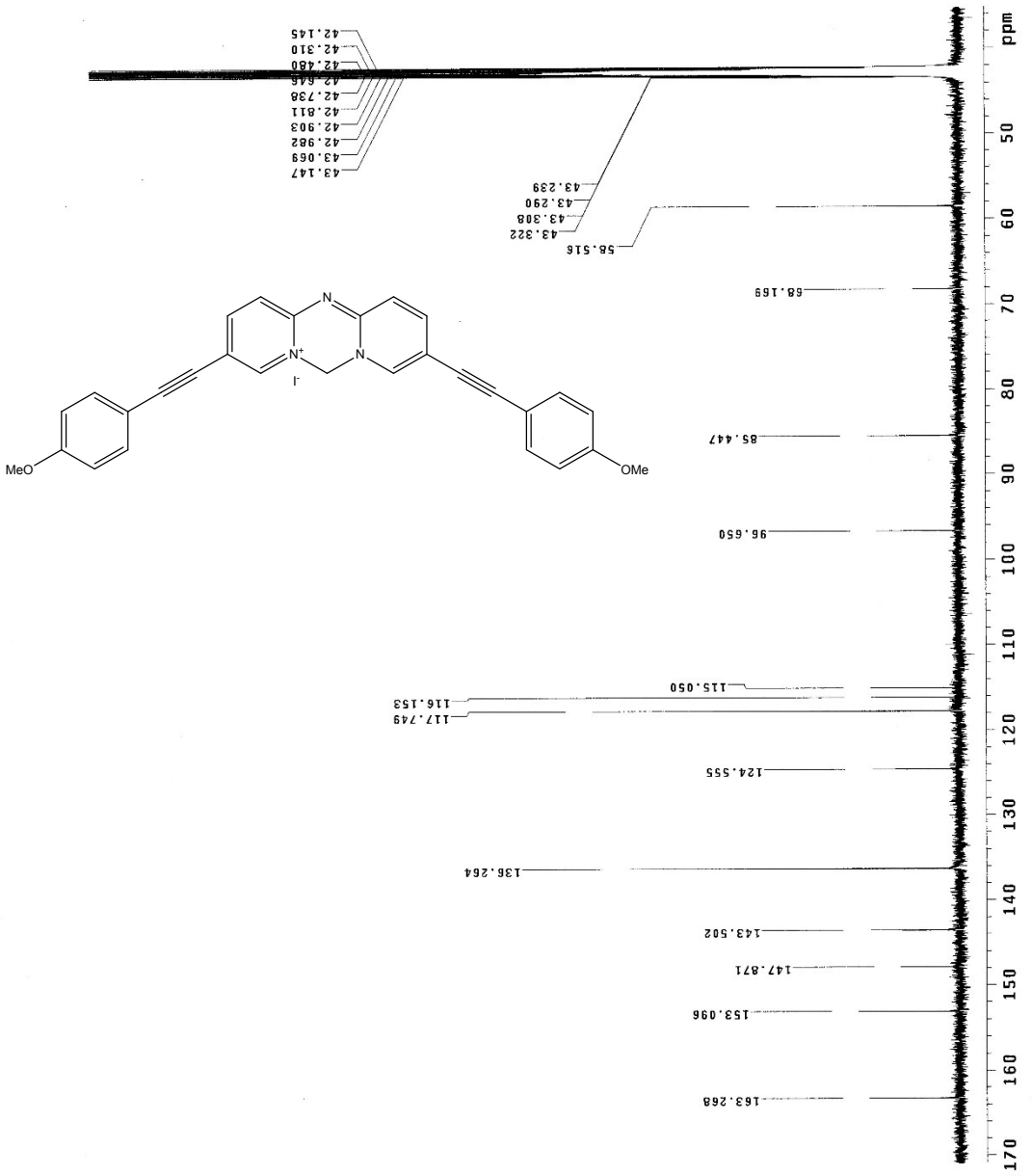
1.045
2.502
2.504
2.508
3.343
3.816
6.423
7.028
7.045
7.286
7.305
7.525
7.543
8.089
8.093
8.111
8.486
8.490
0.25
35.05
3.45
1.10
2.17
1.03
2.02
1.00
1.06


MeO
OMe
I-
N+
N
N
ppm
42.145
42.310
42.480
42.646
42.738
42.811
42.903
42.982
43.069
43.147
43.239
43.290
43.308
43.322
58.516
68.169
85.447
96.650
115.050
116.153
117.749
124.555
136.264
143.502
147.871
153.096
163.268

References:

1 Gaussian 09, Revision B.01, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.; Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J.A.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, O.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J.; Gaussian Inc., Wallingford CT, **2010**.

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